AFRL-RX-TY-TP-2010-0105

Acyclic *N*-Halamine Polymeric Biocidal Films

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Grant No. FA8650-07-1-5908

AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE

■ **Air Force Materiel Command** ■ **United States Air Force** ■ **Tyndall Air Force Base, FL 32403-5323**

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
07-Jul-2010	Journal Article - POSTPRINT	12-APR-2009--24-OCT-2009

4. TITLE AND SUBTITLE

Acyclic N-Halamine Polymeric Biocidal Films (POSTPRINT)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

FA8650-07-1-5908

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

X0C2 (QL102002)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Departments of Chemistry and Biochemistry*, Polymer and Fiber Engineering^, and Nutrition and Food Science#
Auburn University
Auburn, AL 36849

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory
Materials and Manufacturing Directorate
Airbase Technologies Division
139 Barnes Drive, Suite 2
Tyndall Air Force Base, FL 32403-5323

10. SPONSOR/MONITOR'S ACRONYM(S)

AFRL/RXQ

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

AFRL-RX-TY-TP-2010-0105

12. DISTRIBUTION/AVAILABILITY STATEMENT

DISTRIBUTION A. Approved for public release; distribution unlimited.
Available only to DTIC users. U.S. Government or Federal Purpose Rights License.

13. SUPPLEMENTARY NOTES

Distribution Code 20: JOURNAL ARTICLES; DTIC USERS ONLY. Document contains color images. Published in Journal of Bioactive and Compatible Polymers (2010) 25:392-405.

14. ABSTRACT

10%, 20% and 40% concentrations of acyclic amide monomers, methacrylamide (MAM) and acrylamide (AM), were copolymerized with vinyl acetate (VAc). No significant differences between the synthesized copolymers and polyVAc were seen by proton nmr, FTIR and DSC analysis. Biocidal films formed by coating the copolymers onto polyester transparency slides and polyester fabric swatches were chlorinated by exposure to sodium hypochlorite solutions. Both S. aureus and E. coli O157:H7 were completely inactivated within 1 minute on the transparency slides and polyester fabric swatches derived from poly(VAc-co-MAM). The chlorine on the films was stable under UVA irradition and the surfaces were rechargeable upon chlorine loss.

15. SUBJECT TERMS

antimicrobial, bacteria, biocidal coatings, biofilms, N-halamine

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Joe Wander
U	U	U	UU	14	19b. TELEPHONE NUMBER *(Include area code)* 850 283-6240

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Prescribed by ANSI Std. Z39.18

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ABSTRACT: Low concentrations of acyclic amide monomers, methacrylamide (MAM) and acrylamide (AM), were copolymerized with vinyl acetate (VAc). No significant differences between the synthesized copolymers and poly(VAc) were seen by ^{1}H-NMR, FTIR, and DSC analysis. Biocidal films, formed by coating the copolymers onto polyester transparency slides and polyester fabric swatches, were chlorinated by exposure to sodium hypochlorite solutions. Both *S. aureus* and *E. coli* O157: H7 were completely inactivated within 1 min on the transparency slides and polyester fabric swatches derived from poly(VAc-co-MAM). The chlorine on the films was stable under UVA irradiation and the surfaces were rechargeable upon chlorine loss.

KEY WORDS: biocidal coatings, bacteria, N-halamine, biofilms, antimicrobial.

INTRODUCTION

A variety of antimicrobial organic materials, including phosphonium salts [1–4], quaternary ammonium salts [2–17], and cyclic

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0883-9115/10/04 0392–14 $10.00/0 DOI: 10.1177/0883911510370387

N-halamine compounds [18–46], are used as disinfecting agents in areas, such as water purification, medical devices, food packaging, and health-related products. Among these, organic materials made from N-halamines are the most promising candidates for use in manufacturing antimicrobial materials due to their high biocidal efficacy, stability for long-term use, and regeneration following exposure to washing cycles.

Recently, extensive efforts have been made to develop polymeric biocides derived from N-halamines. The addition of N-halamine moieties or N-halamine polymers to the host polymers before polymer processing or fiber extrusion has produced antimicrobial polymers [18,19]. However, if the added compound is water-soluble, there is a potential leaching problem, which could cause adverse environmental issues. A preferable method is to graft [20–22] or coat [23–36] N-halamine precursor monomers onto natural and synthetic polymers with, or to modify polymer units by chemical reaction to form N-halamine derivatives [37–43].

Another approach, to produce biocidal polymers, is to polymerize N-halamine precursor monomers or to copolymerize N-halamine precursor monomers with other common monomers [44–46]. For example, Sun et al. synthesized cyclic-amine monomers and copolymerized them with acrylic and vinyl monomers to produce water insoluble antimicrobial polymers [44–46]. The copolymers derived by incorporating small amounts of cyclic-amine monomers with vinyl acetate formed films on solid surfaces, such as medical devices. All of the cyclic N-halamines containing amine, amide, and imide moieties demonstrate significant efficacy against a broad spectrum of microorganisms [29–34]. Acyclic N-halamines containing these moieties could possibly possess the similar antimicrobial functions as the cyclic N-halamines. Recently, acyclic amide monomers were bound onto cotton and hydroxylated polypropylene by grafting [47–49]. Upon chlorination with dilute household bleach, the grafted methacrylamide (MAM) and acrylamide (AM) side chains on the polymers became acyclic N-halamines, and the biocidal functions were durable and rechargeable.

In general cyclic N-halamine polymers are preferable to acyclic ones to produce antimicrobial surfaces because of their superior halogen stability [50]. In this study, commercially available acyclic amide monomers, methacrylamide and acrylamide, were copolymerized with vinyl acetate to evaluate the potential of acyclic N-halamine polymers as disinfectants. These monomers were chosen for copolymerization because they are relatively inexpensive and vinyl acetate is easily copolymerized with other monomers to produce high-quality films. Small amounts of acyclic amide monomers were added during copolymerization to retain the properties of poly(vinyl acetate) while

providing the copolymers with sufficient amide groups that are necessary for the antimicrobial function upon chlorination. The copolymers were dissolved in acetone and coated onto polyester transparency slides and polyester fabric swatches. The UVA light stabilities and antimicrobial properties of acyclic N-halamine copolymer films on these solid surfaces were investigated.

MATERIALS AND METHODS

Materials

Monomeric acrylamide was purchased from Sigma-Aldrich (Saint Louis, MO). Monomeric vinyl acetate and initiator 2,2′-azobis(2-methylpropionitrile) (AIBN) were obtained from Aldrich Chemicals (Milwaukee, WI). Monomeric methacrylamide was purchased from Acros Inc. (Morris Plains, NJ). All chemicals were used without further purification. Polyester fabric was purchased from a local outlet store.

Instruments

The ^{1}H NMR spectra of the synthesized compounds were recorded with a Bruker AV-400 (400 MHz) spectrometer. Thermal analysis of the synthesized copolymers was conducted by differential scanning calorimetry (DSC) (DSC Q2000, TA Instruments); 5–10 mg samples were scanned from 30°C to 350°C at a heating rate of 10°C/min under nitrogen atmosphere. Molecular weights of the polymers were measured via a modular gel permeation/size exclusion chromatography system, configured of Viscotek ve1122 Solvent Delivery System, Viscotek $GMH_{H\ R}$-M type Column in size $7.8 \times 300\ mm^2$, Viscotek ve3580 Refractive Index Detector, and Viscotek 270 Dual Detector (equipped with a light scattering detector and viscometer). Tetrahydrofuran was used as a solvent and circulated through the system with a flow rate of 1 mL/min. 10 μL of sample solution, at concentrations of 3–6 mg/mL, were used for the tests. The OmniSEC software program was used to analyze the collected multiple detection data.

Synthesis of Copolymers

MAM (0.284 g, 3.34 mmol) and 5.68 g (66.6 mmol) VAc (1 : 20 mole ratio) were added to 1.5 mL of ethanol in a 50 mL flask. AIBN (0.06 g, 1 wt%) was added and the solution was bubbled with N_2 for 10 min.

The flask was sealed and the solution, under constant stirring, was heated at 75–80°C for 2.5 h. The ethanol and residual monomer were removed by extensive rinsing with distilled water and then at reduced pressure. The polymer was dissolved in 30 mL of acetone and after filtering the mixture, the acetone was removed by evaporation to obtain pure white solid copolymers. Different mole ratios (1 : 10; 1 : 20; 1 : 40) of MAM or AM to VAc were used to synthesis a series of copolymers.

Preparation of Copolymer Films on Transparency Slides and Polyester Fabric Swatches

The copolymer was dissolved in acetone at different concentrations (from 2.5 to 20 wt%). 0.5 mL of polymer solution was coated on transparency slides (5 × 5 cm) followed by evaporation of the solvent. The copolymer film was formed on the surface of polyester fabric swatches by soaking the swatches in the copolymer/acetone solution for 10 min, followed by evaporating the acetone.

Chlorination and Analytical Titration

The polymeric-coated films on the transparency slides and polyester fabrics were chlorinated by soaking in a 10% aqueous solution of sodium hypochlorite (0.6% active chlorine NaOCl) at pH 7 at ambient temperature for 1 h. The chlorinated samples were rinsed thoroughly with distilled water and dried at 45°C for 1 h to remove occluded free chlorine. An iodometric/thiosulfate titration method [33,34] was used to determine the chlorine contents of the samples. The chlorine loadings of the films on the slides were calculated with the following equation:

$$Cl^+(\text{atoms/cm}^2) = \frac{N \times V \times 6.02 \times 10^{23}}{2 \times S} \quad (1)$$

where N and V are the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and S is the area of the film in cm^2.

The Cl^+% on the polyester swatches was calculated according to the following equation:

$$Cl^+\% = \frac{N \times V \times 35.45}{W \times 2} \times 100 \quad (2)$$

where Cl^+ (%) is the weight percent of oxidative chlorine on the swatches, N and V are the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and W is the weight of the polyester swatches in grams.

Biocidal Efficacy

Both chlorinated and unchlorinated polymeric films and coated polyester fabrics were challenged with *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* O157:H7 (ATCC 43895). A 'sandwich test' was used to evaluate the biocidal efficacy. The testing began with the addition of 25 μL of the bacterial suspensions to the centers of 1 in.^{2} slides or swatches in a sterile Petri dish, and with second identical slides or swatches placed upon the first ones held in place by a sterile weight. Different slides and swatches samples were exposed for 1, 5, 10, and 30 min, respectively; they were placed in tubes containing 5.0 mL of sterile 0.02 N sodium thiosulfate to quench all oxidative chlorine. The quenched solutions were diluted with pH 7, 100 μM phosphate buffer, plated on Trypticase soy agar and incubated at 37°C for 24 h. The bacterial colonies were analyzed for biocidal efficacy.

UVA Light Stability Testing

UVA light stabilities of the chlorinated polymeric films were measured using an Accelerated Weathering Tester (The Q-panel Company, Cleveland, OH). The films were placed in the UVA (Type A, 315–400 nm) chamber for times in the range of 1–24 h. After a specific time of exposure to UVA irradiation, the films were removed from the UVA chamber and titrated, or rechlorinated and titrated. Each data point in the tables represents the average of triplicate titrations.

RESULTS AND DISCUSSION

Synthesis and Characterization of Poly(VAc-co-MAM) and Poly(VAc-co-AM)

Monomers, methacrylamide and acrylamide, were copolymerized with vinyl acetate by free radical polymerization. The copolymers (Figure 1) were mainly composed of vinyl acetate units with a small portion of methacrylamide or acrylamide. The molecular weights and distribution indices of the synthesized copolymers and homopolymer are summarized in Table 1. The homopolymer, poly(VAc), was synthesized under the same conditions as the copolymers.

Neither FTIR nor ^{1}H NMR exhibited discernible differences between the copolymers and poly(VAc) due to the low concentrations of the AM and MAM moieties in the copolymers. Sun and Sun [44] have observed the same for even higher copolymer mole ratios (1 : 6) in an acrylonitrile

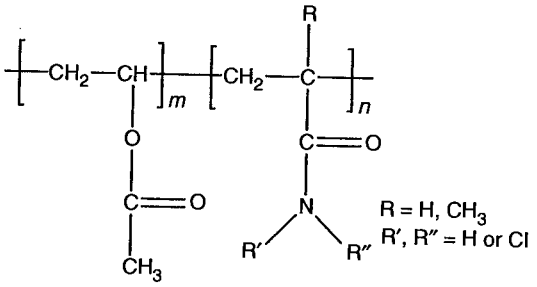

Figure 1. Structures of synthesized copolymers.

Table 1. Molecular weight of poly(VAC-co-MAM), poly(VAc-co-AM), and poly(VAc).

Polymers	Monomers feed ratio (mol : mol)	Mn (Da)	Mw (Da)	Mw / Mn
Poly(VAc-co-MAM)	20 : 1	41,000	80,000	1.95
Poly(VAc-co-AM)	20 : 1	37,000	98,000	2.65
Poly(VAc)	–	49,000	106,000	2.16

copolymer containing a cyclic N-halamine moiety. The ^{1}H NMR spectrum of poly(VAc) was in complete accord with that of Crispin et al. [51], with signals centered at 1.75 (2H), 2.03 (3H), and 4.87 (1H) ppm, corresponding to the methylene, methyl, and methyne protons, respectively. The ^{1}H NMR spectra for the two copolymers were essentially identical to that of poly(VAc) so that actual mole ratios could not be determined. Therefore, the data will be discussed in terms of the feed mole ratios only.

The thermal properties of the copolymers were studied by DSC. The onset of decomposition of poly(VAc-co-AM) and poly(VAc-co-MAM) were almost the same as that for pure poly(VAc) (240–250°C). These results indicate that the addition of a small amounts of AM or MAM during polymerization does not significantly change the thermal behavior of the polymeric vinyl acetate.

Preparation of Biocidal Films

The copolymer poly(VAc-co-MAM) was synthesized with different feed mole ratios of VAc to MAM (10 : 1, 20 : 1, and 40 : 1). The copolymer solutions were prepared in acetone with concentrations of 2.5, 5, 10, and 20 wt%. The polymer solutions were coated onto sample transparency slides and the chlorine loadings of poly(VAc-co-MAM) films on these transparency slides are shown in Table 2. The chlorine weight percent

increased with the increase of mole ratio of amide monomer to vinyl acetate. The increased concentrations copolymer solutions also gave higher chlorine loadings. Although the copolymer synthesized by a feed mole ratio 10 : 1 achieved the highest chlorine loading on the film, the quality of the films coated on the polyester transparency slides were not as good as those from mole ratios of 20 : 1 and 40 : 1. To optimize the chlorine loading on the surface of the films, the 20 : 1 feed mole ratio was employed in the polymerization and a 20 wt% copolymer solution was used for the coatings. The chlorine loading of poly(VAc-co-AM) films on the transparency slides is shown in Table 3; the higher the concentrations of copolymer coincided with higher chlorine loading. The 20 wt% copolymer solutions were also used for coating the polyester fabric swatches.

Biocidal Testing

The chlorinated and unchlorinated films were challenged with the Gram-positive bacterium *S. aureus* and the Gram-negative bacterium *E. coli* O157:H7 by using a 'sandwich test.' The test results are listed in Tables 4 and 5. The copolymer films coated onto polyester transparency slides had greater efficacy in inactivating the bacteria after chlorination

Table 2. Chlorine loading of polyester transparency slides coated with different concentrations of poly(VAc-co-MAM) and different feed mole ratios.

	Cl^+ (atom/cm^2)		
Conc. of copolymer in acetone (%)	10 : 1	20 : 1	40 : 1
2.5	1.0×10^{17}	2.3×10^{16}	2.3×10^{16}
5	3.18×10^{17}	7.1×10^{16}	3.8×10^{16}
10	1.04×10^{18}	2.17×10^{17}	1.22×10^{17}
20	1.44×10^{18}	4.61×10^{17}	2.41×10^{17}

Table 3. Chlorine loading of transparency slides coated with different concentrations of poly(VAc-co-AM) (20 : 1 feed mole ratio).

Conc. of copolymer in acetone (%)	Cl^+ (atom/cm^2) on transparency slides
2.5	4.5×10^{16}
5	9.0×10^{16}
10	2.03×10^{17}
20	4.42×10^{17}

(Table 4), whereas the unchlorinated films produced only a small log reduction for both *S. aureus* and *E. coli* due the adhesion of the live bacteria to the films. The chlorinated films coated with poly(VAc-co-MAM) and poly(VAc-co-AM) inactivated all of the *S. aureus* and *E. coli* within contact times of 1–5 min.

The 20 wt% copolymer concentration in acetone was also coated onto the polyester fabric swatches to determined antimicrobial activity

Table 4. Biocidal tests of poly(VAc-co-MAM) and poly(VAc-co-AM) films against S. aureus and E. coli O157:H7.

Samples	Contact time (min)	Log bacterial reduction	
		S. aureus[a]	*E. coli* O157:H7[b]
Poly(VAc-co-MAM)	30	1.05	0.27
Poly(VAc-co-MAM)-Cl (5.9×10^{17}atoms/cm^2)	1	3.38	6.01
	5	6.05	6.01
	10	6.05	6.01
	30	6.05	6.01
Poly(VAc-co-AM)	30	0.76	0.17
Poly(VAc-co-AM)-Cl (2.5×10^{17}atoms/cm^2)	1	6.05	4.19
	5	6.05	6.01
	10	6.05	6.01
	30	6.05	6.01

[a]Inoculum concentration was 1.13×10^6 CFU per sample.
[b]Inoculum concentration was 1.03×10^6 CFU per sample.

Table 5. Biocidal tests of polyester fabric coated with poly(VAc-co-MAM) and poly(VAc-co-AM) against S. aureus and E. coli O157:H7.

Samples	Contact time (min)	Log bacterial reduction	
		S. aureus[a]	*E. coli* O157:H7[b]
Polyester-poly(VAc-co-MAM)	30	0.94	0.36
Polyester-poly(VAc-co-MAM)-Cl (0.22% Cl^+ wt)	1	6.17	6.00
	5	6.17	6.00
	10	6.17	6.00
	30	6.17	6.00
Polyester-poly(VAc-co-AM)	30	0.34	0.06
Polyester-poly(VAc-co-AM)-Cl (0.18% Cl^+ wt)	1	4.04	6.00
	5	6.17	6.00
	10	6.17	6.00
	30	6.17	6.00

[a]Inoculum concentration was 1.47×10^6 CFU per sample.
[b]Inoculum concentration was 1.00×10^6 CFU per sample.

after exposure to household bleach. The unchlorinated control samples caused a small log reduction with a contact of 30 min (Table 5). It is clear that the chlorinated polyester fabrics coated with poly(VAc-co-MAM) inactivated both *S. aureus* and *E. coli* completely with log reductions of 6.17 and 6.00, respectively, within 1 min of contact. In the case of chlorinated polyester fabric swatches coated with poly(VAc-co-AM), *S. aureus* were also completely inactivated with log reduction of 6.17 within 1 min. Although the chlorinated fabrics coated with poly(VAc-co-AM) were unable to achieve a complete inactivation of *E. coli* within 1 min, the log reduction (4.19) of bacteria was significant.

UVA Light Stability Testing

Since the coated films could be exposed to sunlight in practical applications, the stability of the chlorinated poly(VAc-co-MAM) and poly(VAc-co-AM) film coatings under UVA light conditions was investigated (Table 6). The chlorine on the films decreased very rapidly in the first hour of irradiation for both poly(VAc-co-MAM) and poly(VAc-co-AM); only a slight decrease was observed with further irradiation time. There were about 1.21×10^{17} atoms/cm^2 chlorine on the films after 24 h under UVA light irradiation, indicating that the films were still effective in inactivating bacteria. After exposing the films to UVA light for 7 days, most of chlorine was lost (Table 6). It has been observed in our laboratories that a Cl^+ content of only 1.0×10^{16} atoms/cm^2 is sufficient for observable biocidal activity. Generally, outdoor exposure at benchmark climate sites for 42 days is equivalent to 7 days in accelerated weathering tests [52].

Table 6. UVA light stability of poly(VAc-co-MAM) and poly(VAc-co-AM).

	Cl^+ atom/cm^2	
Time (h)	poly(VAc-co-MAM)	poly(VAc-co-AM)
	4.15×10^{17}	4.35×10^{17}
1	1.60×10^{17}	1.72×10^{17}
2	1.44×10^{17}	1.58×10^{17}
3	1.26×10^{17}	1.51×10^{17}
5	1.21×10^{17}	1.35×10^{17}
24	9.0×10^{16}	1.26×10^{17}
96	6.3×10^{16}	6.8×10^{16}
168	5.0×10^{16}	6.3×10^{16}
168 Rechlorination	3.50×10^{17}	3.97×10^{17}

These films were rechlorinated with an aqueous solution of sodium hypochlorite. The titration results show that 84% and 91% of chlorine on the poly(VAc-co-MAM) and poly(VAc-co-AM) films, respectively, were regained after one cycle. The data indicate that the N–Cl bonds of acyclic N-halamine copolymers and the acyclic N-halamine copolymers themselves are quite stable toward UVA light irradiation. These results are similar to those observed for several cyclic N-halamine siloxanes coated onto cotton fibers [36]; analogous data are not available for polyester transparency slides.

CONCLUSIONS

The copolymers were successfully synthesized with vinyl acetate and a limited amount of acyclic amide monomers. The small amount of amide monomers did not significantly affect the structure or thermal properties of the copolymers compared with the VAc homopolymer. Thin films of the copolymers were coated onto the surfaces of transparency slides and polyester fabric swatches. The chlorinated films demonstrated high biocidal efficacy against *S. aureus* and *E. coli* O157:H7 with about 6 log reductions within a contact time range of one to 5 min. The acyclic N-halamine copolymers were very stable under UVA light irradiation; most of the lost chlorine could be reinstated upon exposure to diluted household bleach.

ACKNOWLEDGMENT

The authors acknowledge the support of the US Air Force through grant FA8650-07-1-5908.

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